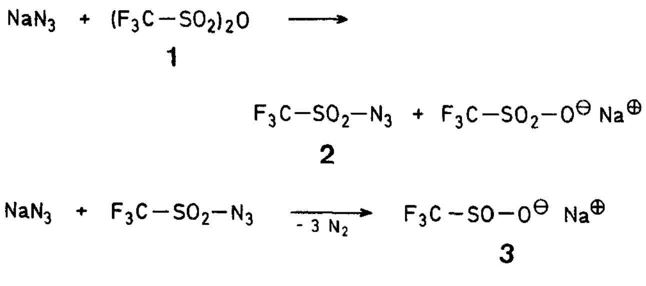
A Simple Preparation of Anhydrous Trifluoromethanesulfinate (Triflinate) Salts and Synthesis of Trifluoromethyl Sulfones (Triflones)

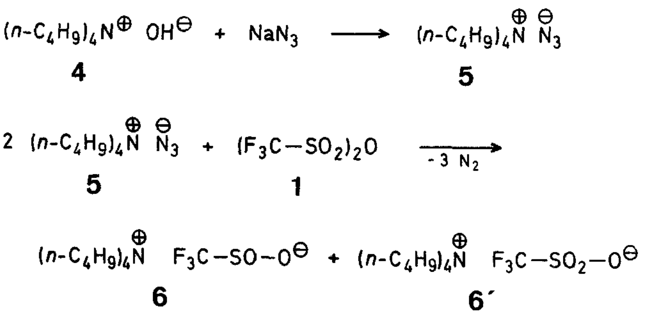
James B. HENDRICKSON, Deborah A. JUDELSON, Toni CHANCELLOR

Edison Research Laboratory, Brandeis University, Waltham, Massachusetts 02254, U.S.A.

As one of the strongest electron-withdrawing groups known, the trifluoromethanesulfonyl (trifyl) group is a versatile functionality for organic synthesis[1]. Trifluoromethyl sulfones (triflones, $R-SO_2-CF_3$) have been prepared either using an electrophilic trifyl source[2] such as triflic anhydride (**1**) or via a displacement on primary halides using a triflinate salt[1]. The latter reaction is uncomplicated but slow. However, the prior preparation of anhydrous triflinate salts has been cumbersome[3,4] and so tends to discourage its general use. The simplest preparation of triflinate salt **3** is the decomposition of trifyl azide (**2**) by azide ion[5]. While the trifyl azide (**2**) is itself made from azide ion and **1** (Scheme **A**), we concluded that the entire preparation can be done as one operation as shown in Scheme **B** using a quaternary ammonium counterion. The latter allows solubility of the system and provides a more reactive anhydrous triflinate nucleophile.

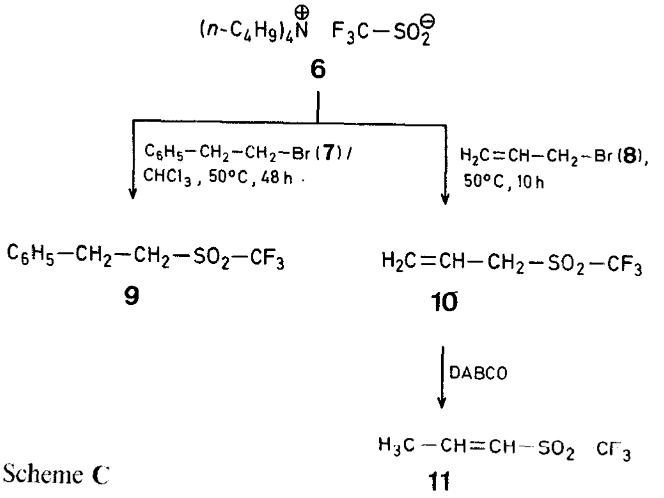


Scheme **A**



Scheme **B**

Thus, tetra-*n*-butylammonium azide (**5**) prepared from tetra-*n*-butylammonium hydroxide (**4**) and sodium azide reacts with triflic anhydride (**1**) in chloroform at −78 °C to give the triflinate anion precursor **6**. The preparation of triflones is illustrated in two representative cases (Scheme **C**); others have been made essentially the same way[6]. Treatment of the mixture **6**/**6′** with β-phenethyl bromide (**7**) or allyl bromide (**8**) gives the corresponding triflones **9** or **10**, respectively. The unreactive triflate anion **6′** in the mixture constitutes no problem in carrying out this reaction. Although acetonitrile as solvent for the reaction may offer somewhat faster rates, the quaternary triflinate **6** reacts 20–40 times faster than the conventional potassium triflinate[4]. The allyl triflone (**10**) is quantitatively isomerized to the conjugated 1-propenyl triflone (**11**) by treatment with a catalytic amount of tertiary amine[6].



Scheme **C**

It is essential not to isolate the trifyl azide intermediate since it is subject to unpredictable explosions[4]. The quaternary azide need not be isolated as below, but its chloroform solution used directly to create the triflinate.

Tetra-*n*-butylammonium Azide (5):

An 40% aqueous solution of tetra-*n*-butylammonium hydroxide (**4**; 250 g, 385 mmol) is washed with dichloromethane (20 ml) to remove any color and then added to a solution of sodium azide (22.8 g, 350 mmol) in water (100 ml). The solution is extracted with chloroform (4 × 75 ml), and the extract dried with magnesium sulfate. Evaporation of the organic phase gives the azide **5** as a white solid; yield: 100 g (99%); but this is unnecessary for preparation of the triflinate **6**.

I.R. (film): ν = 3010 (s), 3000 (s), 2030 (s), 1480 (m), 1380 (m), 880 (w) cm^{-1}.

Tetra-*n*-butylammonium Triflinate/Triflate (6/6′):

A solution of the azide **5** (100 g, 350 mmol) in dichloromethane (500 ml) is cooled to −78 °C. Triflic anhydride (**1**; 49 g, 175 mmol) is slowly added (nitrogen evolution) with stirring. The mixture is then allowed to warm to room temperature and stirred for 3 h. The solution is dried with magnesium sulfate and evaporated to leave a white solid; yield: 106 g (94%).

I.R. (film): ν = 3010 (s), 3000 (m), 1480 (m), 1380 (w); 1250 (s), 1140 (s), 1040 (s), 1020 (s) cm^{-1}.

β-Phenethyl Triflone (9):

β-Phenethyl bromide (**7**; 0.53 g, 2.8 mmol) and the quaternary triflinate/triflate mixture **6**/**6′** (4.37 g, 5.7 mmol) are dissolved in dichloromethane (0.5 ml) and heated at 50 °C for 48 h. The mixture is dissolved in ether (25 ml), washed with water (8 × 25 ml), and dried with magnesium sulfate. Evaporation gives β-phenethyl triflone (**9**) as an oil identical spectrally with an authentic sample[6] and pure by T.L.C. (1 : 1 hexane: dichloromethane, silica gel); yield: 0.49 g (74%).

I.R. (film): ν = 3250–2950, 1620, 1490, 1450, 1360, 1210, 1120 cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$): δ = 2.95–3.22 (m, 2H); 3.36–3.75 (m, 2H); 7.05–7.35 ppm (m, 5H).

Allyl Triflone (10):

Allyl bromide (**8**; 1.03 g, 8.6 mmol) and the quaternary triflinate/triflate mixture **6**/**6′** (13.1 g, 17.1 mmol) are combined without solvent and heated to 50 °C with stirring for 10 h. Vacuum transfer at 50 °C/0.1 torr gives **10**; yield: 1.48 g (98%).

I.R. (CDCl$_3$): ν = 1360, 1255, 1210, 1120 cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$): δ = 4.0 (d, 2H, J = 6 Hz); 5.3–6.3 ppm (m, 3H).

Isomerization of 10 to 1-Propenyl Triflone (11)[6]:

Treatment of a deuterochloroform solution of **10** with a catalytic amount of 1,4-diazabicyclo[2.2.2]octane (DABCO) rapidly yields 1-propenyl triflone[6] (**11**) quantitatively.

^{1}H-N.M.R. (CDCl$_3$): δ = 2.1 (dd, 3H, J = 7.0 Hz, 1.5 Hz); 6.35 (d, 1H, J = 15 Hz); 7.1–7.5 ppm (dq, 1H, J = 7 Hz, 15 Hz).

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Received: July 11, 1983
(Revised form: September 20, 1983)

---

[1] J. B. Hendrickson, A. Giga, J. Wareing, *J. Am. Chem. Soc.* **96**, 2275 (1974).

[2] J. B. Hendrickson, K. W. Bair, *J. Org. Chem.* **42**, 3875 (1977).

[3] J. B. Hendrickson, K. W. Bair, P. L. Skipper, D. D. Sternbach, J. Wareing, *Org. Prep. Proced. Int.* **9**, 173 (1977).

[4] D. A. Judelson, *Ph. D. Thesis*, Brandeis University, 1982.

[5] V. P. Nazaretyan, L. M. Yagupolskii, *Zh. Org. Khim.* **14**, 207 (1978); *C. A.* 88, 151976 (1978).

[6] J. B. Hendrickson, P. L. Skipper, *Tetrahedron* **32**, 1627 (1976).